



TITLE:

Solving the Schrödinger equation of atoms and molecules without analytical integration based on the free iterative-complement-interaction wave function

AUTHOR(S):

Nakatsuji, H.; Nakashima, H.; Kurokawa, Y.;
Ishikawa, A.

CITATION:

Nakatsuji, H. ...[et al]. Solving the Schrödinger equation of atoms and molecules without analytical integration based on the free iterative-complement-interaction wave function. Physical Review Letters 2007, 99(24): 240402.

ISSUE DATE:

2007-12-14

URL:

<http://hdl.handle.net/2433/84646>

RIGHT:

© 2007 The American Physical Society

Solving the Schrödinger Equation of Atoms and Molecules without Analytical Integration Based on the Free Iterative-Complement-Interaction Wave Function

H. Nakatsuji,^{1,2,*} H. Nakashima,^{1,2} Y. Kurokawa,² and A. Ishikawa²

¹Quantum Chemistry Research Institute, Kyodai Katsura Venture Plaza 106, Goryo Oohara 1-36, Nishikyo-ku, Kyoto 615-8245, Japan

²Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

(Received 23 June 2007; published 12 December 2007)

A local Schrödinger equation (LSE) method is proposed for solving the Schrödinger equation (SE) of general atoms and molecules without doing analytic integrations over the complement functions of the free ICI (iterative-complement-interaction) wave functions. Since the free ICI wave function is potentially exact, we can assume a flatness of its local energy. The variational principle is not applicable because the analytic integrations over the free ICI complement functions are very difficult for general atoms and molecules. The LSE method is applied to several 2 to 5 electron atoms and molecules, giving an accuracy of 10^{-5} Hartree in total energy. The potential energy curves of H_2 and LiH molecules are calculated precisely with the free ICI LSE method. The results show the high potentiality of the free ICI LSE method for developing accurate predictive quantum chemistry with the solutions of the SE.

DOI: 10.1103/PhysRevLett.99.240402

PACS numbers: 03.65.Ca, 03.65.Ge, 31.10.+z, 31.15.-p

The Schrödinger equation (SE), $H\psi = E\psi$, provides a governing principle of chemistry, physics, and biology and has an accurate predictive power [1]. For over 80 years since its inception, however, this equation has been thought not to be soluble [1] except for a few special cases. Since 2000, we have been formulating a general method of solving the SE of atoms and molecules in analytical expansion form [2–12]. First, we clarified the mathematical structure of the exact wave function and proposed a method, called the iterative complement (or configuration) interaction (ICI) method, that gives a series of functions converging to the exact wave function [2,3]. This has been confirmed by applying the method to the model harmonic oscillator [4] and to the finite-basis expansion [5]. However, this method includes the integrals of higher powers of the Hamiltonian, which diverge when the Hamiltonian involves singular operators like the Coulomb potential [6,7]. This problem, called the *singularity problem*, always occurs when we apply the method to atoms and molecules. However, this difficulty has been solved by introducing the inverse Schrödinger equation [6] and the scaled Schrödinger equation (SSE) [7,10]. The method based on the SSE was easier and more general.

The SE has the freedom to be written as the SSE [7],

$$g(H - E)\psi = 0, \quad (1)$$

where the scaling function $g(r)$ is positive everywhere and can be zero only at the singular point to scale the singularity to be finite. The simplest ICI (SICI) based on the SSE

$$\psi_{n+1} = [1 + C_n g(H - E_n)] \psi_n \quad (2)$$

is guaranteed to converge to the exact wave function without encountering the singularity problem for the existence of the g function [7,10]. Next, we define the *free ICI* wave function as follows. We collect all the independent functions in the right-hand side of Eq. (2) as $\{\phi_i\}^{(n)}$

($i = 1, \dots, M_n$), which we call complement functions, and give an independent coefficient to each as [7,10]

$$\psi_{n+1} = \sum_{i=1}^{M_n} c_i \phi_i. \quad (3)$$

This free ICI wave function converges faster, for an increased freedom, than the original SICI to the exact wave function. In the free ICI method, the g function can be chosen more freely than in the original ICI: when diverging terms appear, they are simply thrown out, since they are physically not acceptable as elements of the wave function. Starting from appropriate g and ψ_0 , and increasing the order n , one gets the free ICI wave function having an essentially exact structure. By exact structure, we mean that after the variables $\{c_i\}$ are determined by the method equivalent to the SE, the wave function becomes exact.

When we apply the variational principle to the free ICI wave function, we obtain a secular equation that involves the Hamiltonian and overlap integrals. When analytic integrations of these terms are possible, the variational principle gives very accurate results. Actually, we could calculate quite accurate wave functions of helium [12], hydrogen molecule [11], etc.; for helium, the free ICI method gave the energy correct to 40 decimal figures in comparison with 36 of the published result of Schwartz [13]. For H_2 , the result given below is more accurate than before [11,14]. These are the numerical proofs of the accurateness and effectiveness of the free ICI method.

However, different from differentiations, analytic integrations are not always possible, in principle, for arbitrary analytic functions. This is true also for the ICI complement functions. Numerical integration methods are usually insufficient for accuracy and computational cost. We call this difficulty *integration difficulty* because, without solving this difficulty, we cannot apply the present methodology

to general atoms and molecules. The purpose of this communication is to show a solution to this problem. We will use the SE directly instead of the variational principle. Our strategy lies in the constancy of the local energy for the exact wave function.

Local energy of H_2 .—Previously, we reported the free ICI variational calculations of H_2 of order 4 [11]. We have performed here the same calculations to order 5, which consisted of 6776 functions and gave the energy $E = -1.174\,475\,931\,400\,027$ a.u., which is lower than the energy $E = -1.174\,475\,931\,399\,840$ a.u. of Sims and Hagstrom [14], who used 7034 James-Coolidge type functions. So, the present free ICI wave function is variationally best. The structures of the two wave functions are similar, but ours has a bit larger freedom, so that it could give a better result [11]. We showed previously that the free ICI wave function satisfied accurately both nuclear and electron cusp conditions. We show here that it also satisfies the local energy relation, $H\psi(r)/\psi(r) = E_{\text{exact}}$, i.e., the SE itself, at any coordinate r except for the regions very near the nucleus or another electron. Figure 1 shows the local energy plots, when one electron is at the center of the two protons at $z = \pm 1.4011/2$ a.u. and the other moves 1 a.u. apart from the H-H axis. The local energy for $n = 5$ is essentially constant everywhere on this axis and is within $-1.174\,47 \pm 0.000\,01$ a.u. This shows that the free ICI method gives not only accurate energy but also accurate wave function even locally. This result also constitutes a supporting basis for developing the LSE method below.

LSE method.—Precisely, the SE is a local equation: $H\psi(r_\mu) = E\psi(r_\mu)$ stands at any coordinate r_μ in atoms and molecules. Suppose that there are M unknown parameters in the ψ that has an exact structure. Then, we take M independent sampling points, $\mu = 1, \dots, M$, in the coordinate space, which gives M independent simultaneous equations that connect these M variables. Therefore, in principle, these M variables can be determined. Note that this argument is possible only when the wave function we are dealing with has an exact structure, or is potentially exact, so that its local energy can be assumed to become flat and E_{exact} everywhere; the SE itself is satisfied. Our

free ICI wave function is certainly potentially exact, when the order n is large. We have already seen in Fig. 1 that the local energy of the free ICI wave function of H_2 is flat and E_{exact} in high accuracy for $n = 5$.

Inserting Eq. (3) into the SE, we obtain

$$\mathbf{A}\mathbf{C} = \mathbf{B}\mathbf{C}\mathbf{E}, \quad (4)$$

where $\{A_{\mu i}\} = \{H\phi_i(r_\mu)\}$, $\{B_{\mu i}\} = \{\phi_i(r_\mu)\}$, $\mathbf{C} = \{\mathbf{c}^0, \mathbf{c}^1, \dots\}$, and \mathbf{E} is a diagonal matrix with the elements, E_0, E_1 , etc. The superscripts 0, 1, etc., denote ground, first excited, etc., states. \mathbf{c}^k is the coefficient vector of the k th state. Both \mathbf{A} and \mathbf{B} are square matrices when we select M sampling points, but highly nonsymmetric.

Multiplying \mathbf{B}^T from the left, we obtain

$$\mathbf{H}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E}, \quad (5)$$

where $\mathbf{H} = \mathbf{B}^T\mathbf{A}$ and $\mathbf{S} = \mathbf{B}^T\mathbf{B}$, which are square matrices. The \mathbf{S} matrix is symmetric and positive definite, and $S_{ij} = \sum_\mu \phi_i(r_\mu)\phi_j(r_\mu)$, which becomes an overlap integral when the sampling covers all the space. Similarly, the \mathbf{H} matrix has the meaning of the Hamiltonian matrix and is almost symmetric. Therefore, Eq. (5) is more easily handled than Eq. (4) as a diagonalization equation. We note that we may multiply \mathbf{A}^T , instead of \mathbf{B}^T , from the left of Eq. (4) and use the resultant equation for calculating \mathbf{C} and \mathbf{E} , which is useful for the relativistic case since it corresponds to the inverse Hamiltonian method [8].

When we use Eq. (5), the number of the sampling points may exceed the number of the variables M . This has merit when we do random sampling where the independence among the sampling points may not be guaranteed. By increasing the number of the sampling points, the matrices \mathbf{A} and \mathbf{B} become rectangular but the matrices \mathbf{H} and \mathbf{S} are the square of dimension M . Note that Eq. (4) is more informative than Eq. (5); for example, one can always get Eq. (5) from Eq. (4), but the converse is not true.

In the applications below, we used the standard Monte Carlo sampling [15]. This does not mean that we solved the variational equation by the Monte Carlo integration method, whose accuracy is generally not good enough. For the nonvariational nature of the present method, the error in the wave function would be of the same order as that in the energy.

Applications to 2 to 5 electron atoms and molecules.—The results of the free ICI LSE calculations are given in Table I. The calculations were performed in two steps: first, the free ICI complement functions $\{\phi_i\}$ were generated, and then the unknown coefficients $\{c_i\}$ were calculated by the LSE method.

In the first free ICI step, we used the g function of $g = 1 + \sum_{i,A} r_{iA} + \sum_{i<j} r_{ij}$, where A denotes the nucleus and i, j the electrons. The initial function ψ_0 was different for different systems. For helium, we used logarithmic function $\psi_0 = [1 + \ln(r_1 + r_2)] \exp[-\alpha(r_1 + r_2)]$, which describes the effect of three particle interaction near the nucleus [16]. For atoms, the ψ_0 including logarithmic func-

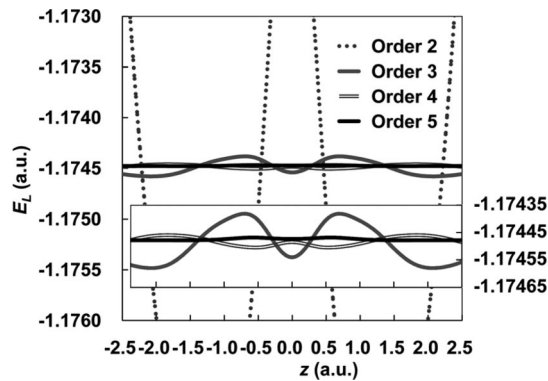


FIG. 1. Local energy plots (with enlargement) for the hydrogen molecule.

TABLE I. Results of the free ICI LSE calculations of small atoms and molecules.

System	Elec.	Order	M_n	Energy (LSE) (a.u.)	Energy (Best ref.) (a.u.)	$\Delta E = \text{LSE-Best ref.}$	Ref.
He	2	6	100	-2.903 724 52	-2.903 724 37	-1.5×10^{-7}	[17]
Li ⁺	2	6	100	-7.279 914 33	-7.279 913 41	-9.2×10^{-7}	[18]
H ₂	2	5	388	-1.174 474 77	-1.174 475 93	1.2×10^{-6}	[11,14,17]
HeH ⁺	2	5	388	-2.978 718	-2.978 706	-1.2×10^{-5}	
Li	3	6	1496	-7.478 043	-7.478 060	1.7×10^{-5}	[17,19]
Be ⁺	3	6	1496	-14.324 753	-14.324 763	1.0×10^{-5}	[20]
He ₂ ⁺	3	6	2632	-4.994 646	-4.994 644	-2.0×10^{-6}	[17]
Be	4	4	1770	-14.667 300	-14.667 355	5.5×10^{-5}	[17]
B ⁺	4	4	1770	-24.348 847	-24.348 883	3.6×10^{-5}	[17]
LiH	4	4	2645	-8.070 516	-8.070 553	3.7×10^{-5}	[17]
B	5	4	15 038	-24.653 872	(-24.653 93)	(5.8×10^{-5})	[21]

tions gave fast convergence [12], so that we used them for the atoms except for B, for which we used a double-zeta initial guess for the $1s$ core. For molecules, the covalent plus ionic initial function was used because it gave better convergence than the covalent-alone one. For H_2 , the covalent function is defined by $\psi_0^C = \exp(-\alpha r_{1A}) \times \exp(-\alpha r_{2B})$ and the ionic one by $\psi_0^I = \exp(-\alpha r_{1A}) \times \exp(-\alpha r_{2A})$. These expressions are shorthanded: we imposed all the symmetries before calculations. For He_2^+ only the covalent function was used.

In the second step, the variables $\{c_i\}$ were determined by the LSE method. The present calculations were done with the HS matrix method, Eq. (5), and the numbers of the sampling were $\sim 10^7$. Since we did not constrain any cusp conditions, we did not sample the points in the region near the nucleus or another electron, $r \leq 0.03/Z$, where Z is the charge of the nucleus or electron. We calculated the wave function, energy, and H -square error (variance) σ^2 that is zero for the exact wave function. At the final stage of the sampling, we calculated σ^2 10 times at a fixed interval and took the minimum σ^2 data as the final result.

The free ICI LSE calculations were done for two- to five-electron closed- and open-shell atoms and molecules and compared with the very accurate reference data [17–21]. For B, the value in parentheses is the estimated exact energy [21]. Table I shows that the present method is highly accurate, the energy errors being less than 6×10^{-5} Hartree (0.04 kcal/mol). This is remarkable, since the present method involves no analytic integration at all. The order of ICI must be larger than 4 for getting sufficient chemical accuracy. The numbers of the complement functions, M , were small. Though we used standard Monte Carlo sampling, we will examine a more efficient method.

Thus, being free from the integration difficulty, the present free ICI LSE method has a high potentiality as a useful tool for calculating accurate analytic solutions of the SE of general atoms and molecules. This is necessary for building up a new frontier of quantum chemistry as accurately predictive science.

For the small systems shown in Table I, very accurate reference data of the exact energy were available in the literature. However, for systems with a larger number of electrons, very accurate reference data are scarcely available [17]. Therefore, to examine the accuracy of the calculated results, an accurate theory of error bars would become necessary in future [22].

Now, let us compare the present method with the full CI, which was the only one available as the general method of solving the SE within finite-basis space. Table II gives a comparison for Be and LiH [23]. The basis sets used in the full CI were quite extensive including up to f and g functions, but the energy error ΔE was 6.6 kcal/mol for Be and 0.76 kcal/mol for LiH. Though the full CI requires a very large number of variables, the solutions are usually far from the true solutions of the SE because of the incompleteness of the basis sets. This is a reason why we need an analytical theory for solving the SE.

Potential curves of H₂ and LiH.—In chemistry, potential energy curves provide basic information on the structures, spectroscopy and chemical reactions of molecules. Here, we apply the present free ICI LSE method for calculating accurate potential energy curves of H₂ and LiH. The initial functions, the free ICI complement functions, and their exponents (1.2 for H₂) were the same as in Table I for all the internuclear distances, R .

TABLE II. Comparison of full CI and free ICI LSE calculations for 4-electron Be and LiH with ΔE being the energy error.

	Best energy (a.u.)	Full CI [23]				Free ICI LSE			
		Basis set	Dimension	Energy (a.u.)	ΔE	n	M	Energy (a.u.)	ΔE
Be	-14.667 355	$9s9p5d3f2g$	3.1×10^6	-14.656 767	1.1×10^{-2} a.u. 6.6 kcal/mol	4	1770	-14.667 300	5.5×10^{-5} a.u. 0.034 kcal/mol
LiH	-8.070 553	$11s8p6d1f$ $/9s8p6d1f$	4.45×10^7	-8.069 336	1.2×10^{-3} a.u. 0.76 kcal/mol	4	2645	-8.070 516	3.7×10^{-5} a.u. 0.023 kcal/mol

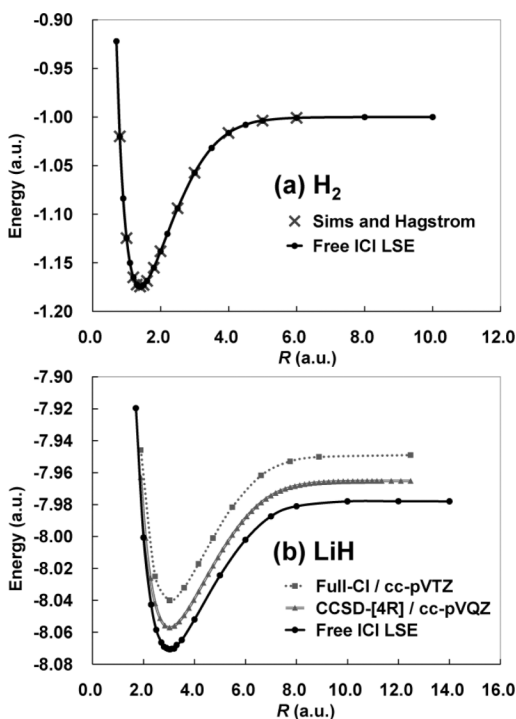


FIG. 2. Free ICI LSE potential curves of (a) H_2 compared with the accurate results [14] and (b) LiH compared with the full CI and multireference CCSD results [24].

Figure 2(a) shows the calculated potential curve of H_2 . The free ICI LSE calculations were done for $R = 0.7$ – 10.0 a.u. We chose many distances to be the same as those of Sims and Hagstrom [14], which permits a direct comparison with their accurate values. The maximum difference was 5.9×10^{-5} a.u. at $R = 0.8$ a.u. The difference decreased gradually as R increased: at $R = 5$ a.u., the difference was 1.3×10^{-6} a.u. Actually, in this accuracy, the present potential curve of Fig. 2(a) overlaps completely with that of Sims and Hagstrom.

Figure 2(b) shows the calculated potential curve of LiH . The calculations were done for 22 different distances from 1.7 to 14.0 a.u. Near the equilibrium distance, 3.015 a.u., we took dense sampling. As R was elongated, the energy approached the sum of the energies of Li and H atoms, -7.9780 a.u. The potential curves of the full CI method and the multireference CCSD method due to Li and Paldus [24] were given for comparison.

Conclusion.—We have shown in this communication that the accurate analytic solutions of the SE can be calculated by the free ICI LSE method without doing analytic integrations over the complement functions. The results calculated with this method were certainly precise. We note that the order n of the free ICI method need not increase as the size of the system increases, since the order is related to the number of electrons ($2n$ electrons) directly correlated to each other.

Since the present free ICI LSE method is general, having no essential difficulty, it can be formulated for solving the

SE of general atoms and molecules. The problems left are to develop efficient algorithms and computing. We note that this method is suitable for superparallel computers developed and being developed in recent years. This is different from other accurate quantum chemistry codes.

By making the present methodology efficient, we hope we would be able to construct truly accurate and predictive quantum chemistry based on the solutions of the SE. If we can further extend it to a simulation methodology, we would be able to reproduce “nature” itself from the principles of quantum mechanics alone. This is indeed our goal.

Thanks are due for the support from the Grant for Creative Scientific Research from the Ministry of Education, Science, Culture, and Sports of Japan.

*To whom correspondence should be addressed.
h.nakatsuji@qc.ri.or.jp

- [1] P. A. M. Dirac, Proc. R. Soc. A **123**, 714 (1929).
- [2] H. Nakatsuji, J. Chem. Phys. **113**, 2949 (2000).
- [3] H. Nakatsuji and E. R. Davidson, J. Chem. Phys. **115**, 2000 (2001).
- [4] H. Nakatsuji, J. Chem. Phys. **116**, 1811 (2002).
- [5] H. Nakatsuji and M. Ehara, J. Chem. Phys. **117**, 9 (2002); **122**, 194108 (2005).
- [6] H. Nakatsuji, Phys. Rev. A **65**, 052122 (2002).
- [7] H. Nakatsuji, Phys. Rev. Lett. **93**, 030403 (2004).
- [8] H. Nakatsuji and H. Nakashima, Phys. Rev. Lett. **95**, 050407 (2005).
- [9] H. Nakatsuji, Bull. Chem. Soc. Jpn. **78**, 1705 (2005).
- [10] H. Nakatsuji, Phys. Rev. A **72**, 062110 (2005).
- [11] Y. Kurokawa, H. Nakashima, and H. Nakatsuji, Phys. Rev. A **72**, 062502 (2005).
- [12] H. Nakashima and H. Nakatsuji, J. Chem. Phys. (to be published).
- [13] C. Schwartz, Int. J. Mod. Phys. E **15**, 877 (2006).
- [14] J. S. Sims and S. A. Hagstrom, J. Chem. Phys. **124**, 094101 (2006).
- [15] B. L. Hammond, W. A. Lester, Jr., and P. J. Reynolds, *Monte Carlo Methods in Ab Initio Quantum Chemistry* (World Scientific, Singapore, 1994).
- [16] J. H. Bartlett, Phys. Rev. **51**, 661 (1937).
- [17] J. Rychlewski and J. Komasa, *Explicitly Correlated Wave Functions in Chemistry and Physics-Theory and Applications*, edited by J. Rychlewski (Kluwer Academic, Dordrecht, 2003), pp. 91–147.
- [18] A. J. Thakkar and T. Koga, Theor. Chem. Acc. **109**, 36 (2003).
- [19] M. Puchalski and K. Pachucki, Phys. Rev. A **73**, 022503 (2006).
- [20] Z. Yan, M. Tambasco, and G. W. F. Drake, Phys. Rev. A **57**, 1652 (1998).
- [21] F. J. Galvez, E. Buendia, and A. Sarsa, J. Chem. Phys. **122**, 154307 (2005).
- [22] G. Temple, Proc. R. Soc. A **119**, 276 (1928).
- [23] G. L. Bendazzoli and A. Monari, Chem. Phys. **306**, 153 (2004).
- [24] X. Li and J. Paldus, J. Chem. Phys. **118**, 2470 (2003).